

Inhalation Exposure  
of Tarpaulin Fumigation Workers to Methyl  
Bromide in Kern County, California  
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By

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SUMMARY

Inhalation exposure of workers performing methyl bromide fumigations of raisins under tarpaulins was monitored in Kern County in November 1982. A total of three workers were monitored. One worker's inhalation exposure during application was monitored for four consecutive 30 minute intervals. The levels of methyl bromide found ranged from 0.29 ppm to 1.34 ppm. The other two workers removed the tarps from the stacks of bins that had been fumigated a month earlier. These two workers were monitored for two consecutive 37 minute intervals. The concentrations of methyl bromide were below the detectable level (0.006 ppm).

Four air samples were also collected in the work area. These samples were located between the stacks before the application, between the stacks after the application, between the stacks during the application, and eight feet from a stack of bins that had just had the tarps removed. The concentrations of methyl bromide at these locations were all below 0.007 ppm. The air temperature was 16°C during the study.

## INTRODUCTION

Methyl bromide (bromomethane,  $\text{CH}_3\text{Br}$ ) is a broad spectrum pesticide which has a variety of uses as a fumigant, including commodity treatment. It is normally sold as a pressurized liquid. Methyl bromide is extremely hazardous with a inhalation  $\text{LC}_{50}$  of 200 ppm in rats. The permissible exposure limit (PEL) for methyl bromide is 15 ppm over a 8 hour workday 40 hour work week. The short term excursion level (STEL) is 25 ppm for 5 minutes. The ceiling limit is 50 ppm which cannot be exceeded at any time.

## MATERIALS AND METHODS

Air concentrations were measured by drawing air through a charcoal sampling tube with a personal air pump, MSA Model C-210. The air pumps were operated at a maximum flow of approximately 0.2 liters/minute. The sampling tubes for the personal samples were placed in the worker's breathing zone. Tygon tubing connected the charcoal sampling tube to the air pump on the worker's belt. The MSA C-210 air pump is a piston cylinder-displacement pump of known displacement. The number of piston strokes were counted during the monitoring interval and multiplied by the cubic displacement of the cylinder. This yielded the total air volume which was then corrected for barometric pressure and temperature. After each monitoring interval the air tubes were capped, frozen, and transported to the Worker Health and Safety laboratory in Sacramento within forty-eight hours. The method for determination of methyl bromide on charcoal tubes is in Appendix I.

The fumigation site was located on an asphalt parking lot. The raisin bins were arranged in stacks, 4 bins high, 2 wide, and 8 long. A polyethylene tarp was placed over each stack and sealed to the ground with dirt. Methyl bromide was supplied from a metal cylinder. A 7 foot flexible tube ran from the methyl bromide cylinder to the tarp. A 3 foot, metal probe was attached to the tubing. The probe was placed through a hole located at the top of the stacks, and layed on top of a bin. The applicator would set up the equipment, release the proper amount of methyl bromide and move the equipment to the next stack. Five stacks of bins were fumigated.

The applicator was monitored for four consecutive thirty minute intervals starting at the time the tank valve was opened during the first fumigation.

Two workers removing tarps from bins that had been fumigated a month earlier were also monitored. The tarp removal was accomplished in two phases. First, the tarps were pulled away from the bins breaking their seal with the ground. Next, the tarps were pulled off the tops of the stacks, and thrown away. Monitoring took place during the removal of three tarps. Each worker was monitored for two 37 minute intervals. The monitoring interval started at the time workers pulled up the first tarp.

Four area air samples were taken in the work area. The first sample was taken before the fumigation and next to a stack that was ready for the tarp to be removed. The sample was taken at ground level for 28 minutes. The second sample was taken 8 feet from a stack that had just had the tarp removed. The sample was taken 5 feet off the ground for 83 minutes. The third sample was taken next to a stack that has just had the tarp removed. This sample was taken 3.5 feet off the ground for 78 minutes. The fourth sample was taken 8 feet from a stack of bins, 30 minutes after it had been fumigated. The sample was taken for 33 minutes, 5 feet off the ground. The air temperature was 16°C during the study.

## RESULTS

<u>Location</u>	<u>Time On</u>	<u>Concentrations</u>
Applicator, 1st 30 minutes	30 minutes	0.29 ppm
Applicator, 2nd 30 minutes	30 minutes	0.68 ppm
Applicator, 3rd 30 minutes	30 minutes	0.93 ppm
Applicator, 4th 30 minutes	30 minutes	1.34 ppm
Tarp Removal Worker, #1, 1st sample	37 minutes	less than 0.006 ppm
2nd sample	37 minutes	" " 0.006 ppm
Tarp Removal Worker, #2, 1st sample	37 minutes	" " 0.006 ppm
2nd sample	37 minutes	" " 0.006 ppm
8 ft. from stack, 5 ft off the ground 30 minutes after fumigation.	33 minutes	" " 0.006 ppm
Next to stack just after the tarp was removed, 3.5 ft off ground	78 minutes	0.006 ppm
Next to a stack before the tarp was removed, ground level	28 minutes	" " 0.007 ppm
8 ft. from boxes, tarp had just been removed, 5 ft. from the ground	83 minutes	" " 0.006 ppm

## CONCLUSION

The workers in this study use methyl bromide at irregular intervals throughout the year. In this case, when they followed the label instructions and work practices described, their inhalation exposure to methyl bromide was well below the levels considered to be hazardous.

## APPENDIX I

### DETERMINATION OF METHYL BROMIDE ON CHARCOAL TUBES

#### Scope

This method is for the desorption and analysis of methyl bromide from charcoal air sampling tubes. It is intended solely for the use of the California Department of Food and Agriculture, Chemistry Laboratory Services.

#### Principle

Methyl bromide (MeBr) that has been absorbed from the air onto activated charcoal is desorbed from the charcoal with ethyl acetate, diluted as needed and analytically determined by gas chromatography using flame ionization or electron capture detection.

#### Reagents and Equipment

1. Ethyl acetate, nanograde.
2. Analytical grade methyl bromide.
3. Approved and calibrated personal sampling pump.
4. Charcoal tubes--SKC #226-09.
5. Developing vials with teflon liners--SKC #226-02.
6. Assorted microsyringes for preparing standards and gas chromatography.
7. Assorted pipets.
8. Volumetric flasks.
9. Small triangular file for scoring glass tubes.
10. Gas sampling bulb--Supelco 500 ml. with septum (#2-2148).

#### Analysis

Interferences: High humidity may affect trapping efficiency.

1. Score each charcoal tube with a file in front of the first section of charcoal.
2. Break open the tube. Remove and discard the glass wool.
3. Transfer the charcoal in the upstream section to a labeled desorption vial which contains a known amount of nanograde ethyl acetate. 2-4 ml. is suggested. Adding solvent to the charcoal may cause loss of MeBr.

4. Remove and discard the foam partition from the tube.
5. Transfer the second section of charcoal to a second labeled desorption vial which contains a known amount of nanograde ethyl acetate.
6. Allow the samples to desorb for one hour while rotating @30 rpm.
7. Transfer an aliquot to a sample storage vial, label, and freeze until analysis time.
8. Determine by GLC.

#### Determination of Desorption Efficiency

1. Inject a known amount of MeBr (1 microgram to several milligrams) into the charcoal with a syringe and cap the tube with the supplied caps. The tube should be from the same lot that was used for the samples.
2. At least five tubes (preferably at levels covering the expected range) should be prepared in this manner and allowed to stand at least overnight to assure complete adsorption. A blank tube should be treated the same way except that no sample is added.
3. Analyze the tubes by the analytical procedure.
4. Desorption efficiency =  $\frac{\text{Response sample} - \text{response blank}}{\text{Response standard}}$

The standard(s) should be the same amount as injected into the charcoal tubes. This eliminates standard variation errors.

#### Calculations:

1. Determine weight of MeBr present on charcoal tube sections by GLC analysis.
2. Correct this total weight of MeBr by subtracting any blank value present on the blank tube.
3. The corrected weight is divided by the desorption efficiency to obtain the final weight of MeBr present.
4. The volume of air sampled is converted to standard conditions of 25°C and 760 mm Hg.

$$VS = \frac{V \times P \times 298}{760 \times (T+273)}$$

Where

VS = Volume of air at standard conditions.  
 V = Volume of air as measured.  
 P = Barometric pressure in mm Hg.  
 T = Temperature of air in °C.

5. Calculate ppb in air from the above data.

$$\text{ppb (volume basis)} = \frac{\text{ng} \times 24.45}{\text{VS} \times 94.9} = \frac{\text{ng}}{\text{VS}} \times 0.2576$$

24.45 is the mole volume of MeBr at 25° and 760 mm.

94.9 is the molecular weight of MeBr.

#### Gas Chromatographic Conditions:

Gas chromatograph with  $\text{Ni}^{63}$ ,  $\text{H}^3$ , or flame ionization detector.

Temperatures - Injector: 125°C

Detector: Follow manufacturer's suggestions

Column: 20' x 1/8" O.D. nickel tubing  
10% SP-2100 on 100/120 Chromosorb W-HP  
70°C, 10 ml/min  $\text{N}_2$  carrier gas  
MeBr retention time approximately 1.9 minutes

Column: 6' x 2 mm I.D. glass  
80/100 Poropak Q  
130°C, 30 ml/min  $\text{N}_2$  carrier gas  
MeBr retention time approximately 1.4 minutes

Column: 20' x 1/8" O.D. nickel tubing  
10% FFAP on 100/120 Chromosorb W-HP  
70°C, 25 ml/min  $\text{N}_2$  carrier gas  
MeBr retention time approximately 1.9 minutes

#### References

1. NIOSH Manual of Analytical Methods, Second Edition. Method S372. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., 20402.
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